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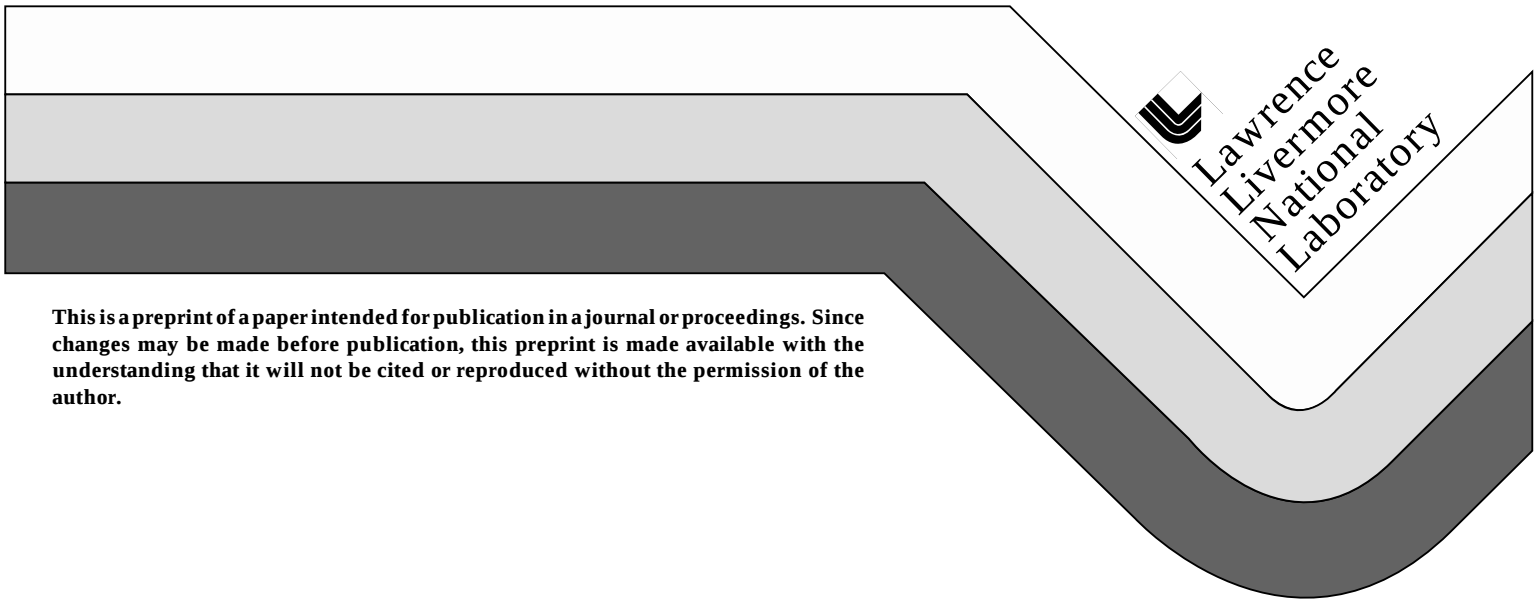

NUMERICAL SIMULATION OF STRONGLY COUPLED BINARY IONIC PLASMAS

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ABSTRACT

New lengthy Monte Carlo simulations of the energy equation of state of binary ionic mixture fluids in a uniform background show that deviations from the linear mixing rule are small, positive, and nearly constant as a function of Γ. Deviations from linear mixing for the Helmholtz free energy are positive and behave as $\ln\Gamma$. Quantitative results are obtained form the correction to the thermonuclear reaction rate.

1. Introduction

In this paper we report results for very accurate numerical simulations of the equation of state (EOS) of binary ionic strongly coupled plasmas at strong coupling in the fluid phase. These results are needed for the determination of phase diagrams for ionic mixtures found in white dwarf star interiors, and to estimate the enhancement of thermonuclear reactions due to ionic screening in very dense stellar interiors. Experimentally it will be possible in a few years to also observe strongly coupled binary ionic mixtures of a finite number of ions in Penning traps as has already happened with the one component plasma (OCP). At the present time, however, the most detailed knowledge of properties of mixtures must come from very long computer simulations, either Monte Carlo (MC) or

molecular dynamics (MD). It has been known since 1977 from the work of Hansen, Torrie, and Viellefosse[1] who solved coupled Hyper-Netted Chain (HNC) equations for ionic mixtures that the EOS of mixtures is given with remarkable accuracy in terms of the EOS of the OCP using the linear mixing rule for the excess Helmholtz free energy, f = F/NkT:

$$f_{mix} = x_1 f_{OCP}(\Gamma_1) + x_2 f_{OCP}(\Gamma_2) + \Delta f \qquad (1)$$

where x_1 and x_2 are the composition fractions by number; thus $x_2 = N_2/(N_1 + N_2) = 1 - x_1$. Differentiation with respect to temperature gives a similar expression which applies to the excess internal energy, u = U/NkT:

$$u_{mix} = x_1 u_{OCP}(\Gamma_1) + x_2 u_{OCP}(\Gamma_2) + \Delta u \qquad (2)$$

and Γ_1 and Γ_2 are the usual coupling parameters:

$$\Gamma_2 = Z_2^{5/3}\Gamma_e \,, \quad \Gamma_1 = Z_1^{5/3}\Gamma_e$$

$$\Gamma_e = e^2/akT \,, \; a = ((4\pi/3)N_e/V)^{-1/3}, \; N_e = Z_1N_1 + Z_2N_2 \qquad (3)$$

The OCP functions, u and f, are known to five figure accuracy from earlier MC simulations[2], and the data for strong coupling ($\Gamma \geq 1$) is reproduced by convenient fitting functions.

The work presented here will be entirely for fluid ionic mixtures; results for solid phase mixtures will appear in a later publication. The fluid results for Δu and Δf in the HNC calculations are positive for all values of the coupling parameters and on the order of a few parts in 10^5 of u and f. The HNC approximation, however, is slightly inaccurate due to the neglect of the bridge functions. Thus complete information about these deviations for linear mixing must come from MC or MD simulations that are accurate to roughly one part in 10^5. This numerical accuracy requirement means that the MC runs have to be significantly longer than any that have been reported so far.

We will focus on results of relatively small values of the composition of the higher Z charge because this is needed for the estimation of the screening function, $H(r) = \beta u(r) + \ln g(r)$, at r = 0 for the calculation of the enhancement of thermonuclear reactions in the strongly coupled fluid phase of some stellar interiors[3,4]. At r = 0 it can be shown that:

$$H(0) = \{F(N_2 = l, \Gamma_2, N - 2, \Gamma_1) - F(N_2 = 0, N, \Gamma_1)\}/NkT$$

$$= [2f_{OCP}(\Gamma) - f(2^{2/3}\Gamma)] - (\partial/\partial x)\Delta f(Z_2 = 2, x, \Gamma_1 = \Gamma)_{x \to 0} \qquad (4)$$

In Eq.4 we use $x_2 = x$. The derivative term represents the deviation from linear mixing, and is expected to be a very small correction to linear mixing term shown above in squre brackets The estimation of this term requires accurate MC results for $Z_2 = 2$, and very small values of x. Computer time expense limits the size of the system that can be simulated to about 1000 charges, so that about the best we can do is $N_2 = 10$ and $N_1 = 990$, or $x = .01$. However, with sufficiently long MC runs to give the needed accuracy we can estimate the size of this correction term.

2. OCP Results for HNC and MC

The HNC equation is a remarkably good approximation to the OCP but not exact because of the neglect of the bridge functions. It is still useful to work with the HNC results, however, because of the property of the HNC approximation that for each Γ in addition to the internal energy one also obtains the value of the Helmholtz free energy[1]. With the MC energy data one must obtain the Helmholtz free energy by means of a temperature integration over several values of Γ starting with the onset of strong coupling at $\Gamma = 1$:

$$F_{ex}/NkT = \int_1^{\Gamma} d\Gamma' \, \Delta(\Gamma') + F_{ex}(\Gamma = 1)/NkT \qquad (5)$$

Results for HNC u and f and MC results for u are shown in Table 1.

The MC results for U/NkT in Table 1 were done with N = 1000 particles and with 200 to 400 x 10^6 configurations so as to obtain accuracy to at least the 4th decimal place. The difference between the MC and HNC results is due to the neglect of the bridge diagrams in the HNC approximation. This difference is very small at $\Gamma = 1$, and is less than 1% even at $\Gamma = 160$. Both the MC and the HNC energy results can be fitted conveniently with the form:

$$u = a\Gamma + b\Gamma^s + c \qquad (6)$$

Table 1, HNC and MC Energy Results for the OCP

Γ	HNC U/NkT, F/NkT	MC U/NkT
1	-0.570455	-0.57205 ± 0.00005
	-0.436484	
$2^{5/3}$		-2.25491 ± 0.00010
5	-3.732075	-3.75696 ± 0.00010
	-3.190834	
10	-7.935439	-7.99837 ± 0.00014
	-7.060678	
15	-12.21718	-12.31729 ± 0.00013
	-11.08607	
20	-16.53774	-16.67327 ± 0.00016
	-15.19177	
$10x2^{5/3}$		-26.98179 ± 0.00022
40	-33.99923	-34.25940 ± 0.00026
	-32.00113	
$20x2^{5/3}$		-54.09648 ± 0.00034
80	-69.26387	-69.72742 ± 0.00041
	-66.37279	
160	-140.15559	-141.03963 ± 0.00069
	-136.1453	

which for the free energy leads to:

$$f = a\Gamma + (1/s)b\Gamma^s + c\ln\Gamma + d \qquad (7)$$

For the MC energies in Table 1 the fitting coefficients are a = -.899126, b = .60712, c = -.27998, and s = .321308 with a standard deviation of $\sigma = \pm .00045$. This is the most accurate fitting function for the OCP energy at the present time. Note that the standard deviation quoted here is for the fit to the actual MC numbers in Table 1, and not the MC statistical errors. These statistical errors increase from ± 0.00005 at Γ = 1 (nine parts in 10^5) to ± 0.00069 at Γ 160 (less that one part in 10^6). It is necessary to have similar accuracy in the MC ionic mixture simulations in order to obtain realistic results for Δu and Δf. The fit given here for N = 1000 particles is distinctly better than the previous best available fit in Ref. 2, a four term fit

with s = 1/3 for much shorter MC runs with N = 686, which gave $\sigma = \pm$ 0.0019.

3. HNC and MC Binary Ionic Mixture Results

In order to obtain definitive results for deviations from linear mixing as defined by Eqs. 1 and 2 from MC it is necessary to have equally accurate results for all three terms in Eq. 1 and to do all three with the same number of particles (we use N = 1000) so as to eliminate any 1/N dependence. This is the reason for strange looking entries in Table 1 such as $\Gamma = 2^{5/3}$. It is a mistake to obtain values of u_{OCP} for Γ_1 and Γ_2 from a fitting function to the OCP energy data unless that fitting function is a fit to OCP data for the same value of N used in the mixture runs, i.e. $N = N_1 + N_2$. In our work we have whenever possible done **three** MC runs for each mixture to obtain Δu, namely the MC energy of the actual ionic mixture and the OCP results for Γ_1 and Γ_2. Our fitting function to the OCP MC data in Table 1, is sufficiently accurate to deal with all mixtures. We also obtained ionic mixture results for the coupled HNC equations even though these results are inevitably less exact than the enormously more

Table 2, HNC and MC Mixture Results for $Z_2 = 2$, $x_2 = .05$

Γ_1	**HNC** u_{mix}, f_{mix}	**HNC** Δu, Δf	**MC** u_{mix}	**MC** Δu
1	-.65283	+.00124	-.65488	+.00134
	-.50533	+.00238	±.00005	±..00006
5	-4.19286	+.00113	-4.22167	+.00134
	-3.61696	+.00429	± .00014	± .00019
10	-8.87605	+.00115	-8.94666	+.00087
	-7.95314	+.00508	± .00013	± .00019
20	-18.44379	+.00112	-18.59212	+.00077
	-17.03229	+.00587	± .00023	± .0028
40	-37.84426	+.00105		
	-35.75743	+.00662		
60	-57.38566	+.00115		
	-54.79354	+.00704		
80	-76.99767	+.00128		
	-73.99449	+.00746		
100	-96.65425	+.00120		
	-93.27965	+.00753		

computer intensive MC results. We obtained HNC free energy mixture results using Eq. 11 in Ref. 1. The use of the HNC mixture equations allows us to obtain a structure for the deviations from linear mixing and to quickly map out the behaviour as a function of the three parameters, Z_2, x_2, and Γ_1. Results for $Z_2 = 2$ and $x_2 = .05$ are given in Table 2.

The striking feature of the HNC results for Δu in Table 2 is its constant value, i.e. no dependence on Γ_1. The immediate consequence using Eq. 5 is that the deviation from linear mixing, Δf, must have the form:

$$\Delta f_{HNC} = a\ln\Gamma_1 + b \qquad (8)$$

where the constants a and b depend on Z_2 and x_2. The HNC results for Δf in Table 2 confirm this logarithmic dependence on Γ_1 very closely with a and b equal to the values of Δu and Δf at $\Gamma_1 = 1$.

The MC result for Δu at $\Gamma_1 = 1$ is in near agreement with the corresponding HNC result (+.00134 ± .00006 vs + .00124) as would be expected. As Γ_1 increases, the MC results for Δu decrease, and Δu can be modelled as:

$$\Delta u_{MC} = a/(1 + c\Gamma_1) \qquad (9)$$

This functional dependence on Γ_1 leads to a free energy deviation of the form:

$$\Delta f_{MC} = a\{\ln\Gamma_1 - \ln(1 + c\Gamma_1)/(1 + c)\} + b \qquad (10)$$

a and b can be taken as the MC values of Δu and Δf at $\Gamma_1 = 1$ and $c \approx .034$. This difference between HNC and MC is a consequence of the increasing influence of the bridge diagrams as Γ_1 increases.

For estimation of the $(\partial/\partial x)\Delta f$ term in Eq. 4 we need MC results for the smallest possible value of x_2 which for practical purposes is $x = .01$ which corresponds to $N_2 = 10$ and $N_1 = 990$. HNC and MC results for Z_2 and $x = .01$ are given in Table 3.

The HNC Δu in Table 3 is again nearly nearly independent of Γ_1 and is about 1/5 of the Δu in Table 2, as expected. The MC results for Δu are marginal, probably because of the small number of $Z_2 = 2$ particles. The negative value of Δu_{MC} at $\Gamma_1 = 10$ is the only negative value of Δu for any mixture that we have run; it is well

Table 3, HNC and MC results for $Z_2 = 2$ and $x_2 = .01$

Γ_1	**HNC** u_{mix}, f_{mix}	**HNC** Δu_{mix}, Δf_{mix}	**MC** u_{MC}	**MC** Δu_{MC}
1	-.58691	+.00026	-.58849	+.00039
	-.45021	+.00052	±.00006	±.00008
5	-3.82422	+.00025	-3.85009	+.00009
	-3.27599	+.00094	±.00012	±.00006
10	-8.12356	+.00026	-8.18830	-.00010
	-7.23912	+.00111	±.00013	±.00019
20	-16.91891	+.00025		
	-15.19177	+.00509		
40	-34.99923	+.00022		
	-32.00113	+.00143		

within the error bars. Based on HNC and MC results in Table 2 and the indication in Table 3 that the coefficients a and b in Eq.8 are proportional to x_2, the correction term needed for the thermonuclear enhancement rate in Eq. 4 is:

$$(\partial/\partial x)\Delta f(Z_2 = 2, x, \Gamma_1 = \Gamma)_{x \to 0} \approx .027 \ln\Gamma + .048 \qquad (11)$$

4. Comparison with OIIVH

Ogata, Iyetomi, Ichimaru, and Van Horn[5] (OIIVH) have done a thorough MC study of the binary ionic mixture for both fluid and solid phases with results for $Z_2/Z_1 = 4/3$, 3, and 5. Their results for the solid mixture phase give Δu_{mix} as positive, but for the fluid phase they find that negative values of Δu_{mix} for several of their mixture runs when $x = .01$ and .05. They find that their fluid Δu values decrease with increasing Γ_1 (for Γ_1 from 5 to 20). They assume a functional dependence of $\Delta u \propto 1/\Gamma_1$, which is far more extreme than our MC results shown in Table 2 indicate. Their energy averages are perfomed over 7×10^6 configurations; our runs are typically 200 to 400×10^6 configurations. Their negative values of Δu have significant consequences for both their phase diagrams and their correction to the thermonuclear reaction rate. Consequently it is important to establish as clearly as possible the positive sign of Δu as well as the magnitude and dependence on Γ_1. In Table I of OIIVH results were presented for 30 fluid mixtures, half with $Z_2 = 3$ and half with $Z_2 = 5$. Of these 30 mixtures they obtained negative values

of Δu for six, four for x = .01 and two for x = .02. We repeated 12 of their mixture runs including the six for which the obtained the negative values of Δu, and a few other values. Our results are shown in Table 4.

Table 4. MC Results for $Z_2 = 3$ and $Z_2 = 5$

			DSC		OIIVH	
Z_2	x	Γ_1	u_{mix}	Δu	u_{mix}	Δu
3	.01	1	-.61332 ±.00004	+.00099 ±.00005		
3	.01	10	-8.45874 ±..00011	+.00060 ±..00018	-8.461± .001	-.004
3	.02	10	-8.91927 ±.00011	+.00104 ±.00018		
3	.01	15	-13.01204 ± .00018	+ .00038 ± .00022	-13.012± .001	-.003
3	.01	20	-17.60188 ± .00026	+.00097 ±.00031	-17.602± .001	-.002
3	.05	1	-.77883 ±.00005	+.00450 ±..00007		
3	.05	10	-10.30053 ±..00014	+.00206 ±..00021	-10.301±.001	.000
3	.05	15	-15.79068 ±..00026	+.00225 ±..00030	-15.791±.001	-.001
3	.05	20	21.31834 ±..00019	+.00281 ±.00026	-21.319±.001	-.001
5	.01	1	-.68345 ±.00004	+.00276 ±.00004		
5	.01	10	-9.20414 ±.00015	+.00144 ±.00021	-9.205±.001	-.002
5	.05	10	-14.02753 ±..00015	+.00688 ±.00022	-14.028±..001	+.004
5	.1	10	-20.05840 ±..00017	.01206 ±.00028	-20.057±..001	+.011
5	.2	10	-32.12399 ±.00023	+.01855 ±..00040	-32.126±.002	+.015
5	.5	10	-68.33913 ±.00032	+.01967 ±..00084	-68.343±.003	+.015

It is clear from Table 4 that the MC u_{mix} results of OIIVH are correct to the accuracy stated, and comparison with the more accurate DSC results is satisfactory. Yet the OIIVH results for Δu are generally lower than the DSC results by .001 to .004, and consequently several of the OIIVH Δu values are negative. The reason for this is that OIIVH computed their linear mixing results using the an OCP fitting function by Ogata and Ichimaru[6] (Eq. 11 in OIIVH). Their fitting function misses the actual OCP values in Table 1 at Γ = 10, 15, and 20 by about .003 to .004. This seemingly small error is enough to give the spurious results for Δu presented in OIIVH and shown in Table 4. Their elaborate fitting functions for Δu and Δf (Eqs. 12 and 16 in OIIVH) are consequently incorrect.

5. Conclusion

The primary conclusion from this analysis of our new MC ionic mixture results is that the deviations are always small and **positive** and are in general agreement with the corresponding HNC results. Our MC results for Δu indicate a slight decrease with increasing Γ, but certainly not $O(1/\Gamma)$ as suggested by OIIVH.
Eq. 9 models our Δu results for Z_2 = 3 and 5 in Table 4 quite well. Consequently Δf is well represented by Eq. 10 with the constants a and b depending only on Z_2 and x. All the MC data can be represented fairly well with Eqs. 9 and 10 using a and b as the values of Δu and Δf at Γ = 1 from HNC.

The construction of phase diagrams for the binary ionic mixture requires Δf for both fluid and solid phases. The Δf results of OIIVH for the fluid mixture are certainly incorrect because of their spurious negative values of Δu. The immediate consequence of our results for Δf is that the azeotropic corner of the OIIVH phase diagrams goes away. For $Z_2/Z_1 < 1.4$ the phase diagram is spindle shaped in agreement with Segretain and Chabrier[7].

With regard to the calculation of thermonuclear reaction rates in stellar interiors we obtained an explicit estimate of the effect of deviation from linear mixing, Eq. 11, which in general is only about .1% of the total value of H(0). The OIIVH result for this correction is closer to 2% in magnitude and of the incorrect sign due to their

negative results for Δu and hence also Δf. For thermonuclear reaction rate calculations the Alastuey and Jancovici[4] procedure is accurate when the improved OCP results for f (Eq. 6 and 7) are used.

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